

PATENT SPECIFICATION

(11) 1433850

10 (21) Application No. 38746/74 (22) Filed 4 Sept. 1974
 5 (31) Convention Application No. 99641/73 (32) Filed 4 Sept. 1973 in (19)
 33 (33) Japan (JA)
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 43 (52) Index at acceptance

1 C7B 1B 1E 1F 1K 1L 1Q 1R 1S 1T 1V



(54) METHOD OF ELECTROPLATING ON A METAL SUBSTRATE

5 (71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to an electroplating method whereby from a single electroplating bath a non-magnetic plated film and a ferromagnetic plated film are selectively deposited.

15 In conventional electronic memory elements having a ferromagnetic thin film, some elements are composed of a ferromagnetic film deposited on a non-magnetic base and other elements additionally have a protective non-magnetic film superplated on the ferromagnetic film. Examples of such memory elements are magnetic discs and magnetic drums for electronic computer use, video discs for video slow-motion and for stationary image reproduction, and magnetic heads.

20 Conventional processes for producing these elements having a non-magnetic film and a ferromagnetic film include the following steps. A non-magnetic film

troplating a non-magnetic metallic coating and a ferromagnetic metallic coating on to a non-magnetic metallic substrate, which comprises immersing said substrate in an aqueous electroplating bath containing at least one salt of one or more ferromagnetic metals, passing an electric current having a current density in the range of 0.3 to 1.5 Amps/dm² between the substrate and a counter electrode in the bath to cause a non-magnetic coating to be deposited, and then increasing the electric current to a current density in the range of 0.8 to 10 (preferably not more than 4.0) Amps/dm² to cause a ferromagnetic coating to be deposited from the same bath.

25 Preferably the electroplating bath contains at least one salt of nickel or cobalt as the salt of the ferromagnetic metal, optionally together with a compound of chromium and/or phosphorus. Nickel salts are most preferred, and with these a phosphorus-containing salt is usually present. The electroplating bath may also contain one or more of compounds of copper, zinc, gold or tin. When these metals are present it is believed

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SPECIFICATION No. 1,433,850

Page 2, line 104, delete Conditions insert
 Conditions
 Page 4, line 43, after ferromagnetic insert
 plated
 Page 5, line 41, after in delete any of Claims
 insert Claim 5, where..

THE PATENT OFFICE
 15th June, 1976

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This invention relates to an electroplating method whereby from a single electroplating bath a non-magnetic plated film and a ferromagnetic plated film are selectively deposited.

In conventional electronic memory elements having a ferromagnetic thin film, some elements are composed of a ferromagnetic film deposited on a non-magnetic base and other elements additionally have a protective non-magnetic film superplated on the ferromagnetic film. Examples of such memory elements are magnetic discs and magnetic drums for electronic computer use, video discs for video slow-motion and for stationary image reproduction, and magnetic heads.

Conventional processes for producing these elements having a non-magnetic film and a ferromagnetic film include the following steps. A non-magnetic film is formed by plating the base in a non-magnetic plating bath (such as a bath for depositing copper, zinc, chromium or gold); a ferromagnetic film is separately formed from another bath (such as a bath for depositing nickel, cobalt or a nickel-cobalt alloy).

However, these conventional plating processes have the defects that two separate baths are required, with a washing step between them to prevent carry-over of the bath solutions, and time is needed for these three steps and for the transferring between the steps; in a factory process, special apparatus is also required for the transfers.

In order to simplify this process we have devised a plating method capable of being carried out in a single plating bath, wherein both a non-magnetic plate film and a ferromagnetic plate film are selectively deposited by varying the plating conditions.

This invention provides a method of elec-

troplating a non-magnetic metallic coating and a ferromagnetic metallic coating on to a non-magnetic metallic substrate, which comprises immersing said substrate in an aqueous electroplating bath containing at least one salt of one or more ferromagnetic metals, passing an electric current having a current density in the range of 0.3 to 1.5 Amps/dm² between the substrate and a counter electrode in the bath to cause a non-magnetic coating to be deposited, and then increasing the electric current to a current density in the range of 0.8 to 10 (preferably not more than 4.0) Amps/dm² to cause a ferromagnetic coating to be deposited from the same bath.

Preferably, the electroplating bath contains at least one salt of nickel or cobalt as the salt of the ferromagnetic metal, optionally together with a compound of chromium and/or phosphorus. Nickel salts are most preferred, and with these a phosphorus-containing salt is usually present. The electroplating bath may also contain one or more of compounds of copper, zinc, gold or tin. When these metals are present it is believed that they selectively deposit in the non-magnetic coating.

When plating a substrate comprising a metal such as copper, zinc or tin, variation of the plating conditions is necessary in order to obtain successively a non-magnetic film and a ferromagnetic film. The plating conditions which can be varied are the manner of charging the plating bath with electricity, the electric current density of the plating bath, the temperature of the plating bath, whether or not the plating bath is stirred and the degree of stirring, and the duration of the plating.

By varying these parameters, it is possible to selectively deposit both a non-magnetic film and a ferromagnetic film in the same bath. However, it is difficult to selectively obtain these films by varying the temperature of a plating bath; variation of the temperature is not so effective because the plating bath temperature must necessarily always be varied. We have found that variation of the electric

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current density is most effective in a plating bath for selectively depositing a non-magnetic film and a ferromagnetic film.

Thus, with an appropriate composition of the plating bath, the electric current density is varied, so that when the current density is low, a non-magnetic film is deposited, and when the current density is high, a ferromagnetic film is deposited. The actual density used will vary depending upon the composition of the plating bath and sizes of the particles in the film to be deposited. The composition of the bath determines the character of the film formed when the current density used is in the intermediate range of 0.8 to 1.5 A/dm².

In order to selectively deposit a non-magnetic and a magnetic film from one plating bath, it is also important to appropriately control the particle size in the film to be deposited, by appropriately varying the plating conditions, especially the current density and the composition of the bath. The sizes of the deposited particles are preferably controlled to 500 Å to 0.1 micron in the ferromagnetic coating and to 100 Å to 0.1 micron in the non-magnetic coating.

The pH of the plating bath can be from 2 to 6. A suitable temperature range is from 10° to 70°C. Electrodes which can be used are a nickel anode plate having a purity of more than 99.9% where a nickel plating bath is used and a platinum- or rhodium-plated (0.1 to 0.5 microns thick plating) copper, tin or zinc plate anode where a cobalt plating bath is used. Suitable plating techniques which can be employed are described in U.S. Patents Nos. 2,644,787, 3,152,974, 3,227,635, 3,578,571 and 3,637,471. Electricity can be supplied to the electrodes as pulses of the same polarity of current, or the polarity of the current applied to the anode and cathode can be alternated.

The substrate may first be provided with a subbing layer (e.g. copper, zinc or tin) before being electroplated by the method according to the invention.

Suitable plating bath compositions for forming such subbing layers of Cu, Zn or Sn on the substrate are as follows:

Bath for plating copper:

CuSO ₄ . 5H ₂ O	1 to 300	g/litre
H ₂ SO ₄	5 to 30	cc/litre

Bath for plating zinc:

ZnSO ₄	1 to 300	g/litre
H ₂ SO ₄	5 to 30	cc/litre

Bath for plating tin:

SnSO ₄	1 to 300	g/litre
H ₂ SO ₄	1 to 30	cc/litre

An exemplary bath for plating nickel by the method according to the invention has the following composition:

NiSO ₄ . 6H ₂ O	10	to 30	g
NiCl ₂ . 6H ₂ O	5	to 15	g
H ₃ BO ₃	5	to 20	g
NaH ₂ PO ₄ . 2H ₂ O	0.1	to 20	g
Pure water	1	litre	

This bath is suitably used at a temperature of 10° to 40°C.

Determination of whether the plated film is non-magnetic or ferromagnetic can be made by detecting the presence of a saturation magnetization (B_m) in a hysteresis curve obtained with a B-H tracer; this test is carried out on a sample of plated film having an area of 1 cm² and a thickness of 0.05 to 0.1 μ.

The method of this invention is much simpler than the afore-described two-bath conventional processes for the plating of two films, and can be carried out more simply and cheaply. The plated articles obtained are useful as electronic memory components having good memory characteristics.

The invention is illustrated by the following Examples.

EXAMPLE 1

Using a plating bath containing the components given in the following Table 1, the bath being provided with a nickel plate anode (nickel purity: 99.9%), a copper plate base substrate (copper purity: 99.9%), which was previously confirmed to be non-magnetic using a B-H tracer, was plated by varying the density of the electric direct current during the plating.

TABLE 1

Composition		
NiSO ₄ . 7H ₂ O	300	g
NiCl ₂ . 6H ₂ O	50	g
H ₃ BO ₃	40	g
NaH ₂ PO ₄ . 2H ₂ O	14	g
Pure water	1000	cc

Bath Conditions

Plating Bath Temperature	45° ± 5°C	105
pH	4.6 ± 0.4	

The plating conditions and the results obtained are given in the following Table 2.

TABLE 2

				Sample			
		1	2	3	4	5	6
5	Plating Conditions:	Electric Current Density (A/dm ²)	0.5	1.2	1.5	2	3
		Plating Time (sec)	60	40	40	40	25
	Existence of Magnetic Character	X	X	0	0	0	0
	Coercive Force: Hc (Oe)	—	—	5	40	80	74
	Squareness Ratio: SQ (Br/Bs)	—	—	0.82	0.78	0.67	0.80

10 Note 0: ferromagnetic
X : non-magnetic

15 From the results contained in Table 2, it is seen that in this plating bath, when the electric current density was 1.5 A/dm² or more, a ferromagnetic plate film was deposited, and when the electric current density was 1.2 A/dm² or less, a non-magnetic plate film was deposited.

20 The saturation magnetization value of the ferromagnetic plate film obtained was 5800 G/cc, and it was confirmed that the film is an excellent nickel-plated film having a saturation magnetization value which approximates to that of pure nickel.

25 EXAMPLE 2

Using a plating bath containing the components given in the following Table 3, the bath being provided with a nickel plate

anode (nickel purity: 99.9%), a zinc plate substrate (zinc purity: 99.8%), which was previously confirmed to be non-magnetic using a B-H tracer was plated by varying the electric current density and the plating time.

	Composition	35
NiSO ₄ · 7H ₂ O	230 g	
NiCl ₂ · 6H ₂ O	45 g	
H ₃ BO ₃	40 g	
NaH ₂ PO ₄ · 2H ₂ O	4 g	
Pure Water	1000 cc	40

Bath Condition
Plating Bath Temperature 50° ± 4°C
pH 4.8 ± 0.4

The plating conditions and the results obtained are given in the following Table 4. 45

TABLE 4

			Sample				
		7	8	9	10	11	12
50	Plating Conditions:	Electric Current Density (A/dm ²)	0.4	0.5	0.6	0.8	1.2
		Plating Time (sec)	60	60	60	90	90
	Existence of Magnetic Character	X	X	X	0	0	0
	Coercive Force: Hc (Oe)	—	—	—	60	124	84
	Squareness Ratio: SQ (Br/Bs)	—	—	—	0.82	0.78	0.87

55 From the results contained in Table 4, it can be understood that in this plating bath, non-magnetic plated films and ferromagnetic plated films were obtained when the electric current density was 0.6 A/dm² or less and 0.8 A/dm² or more, respectively.

plating conditions and the results obtained are given in the following Table 6.

	Composition	70
Ni(BF ₄) ₂	100 g	
H ₃ BO ₃	15 g	
NaH ₂ PO ₄ · 2H ₂ O	4 g	
Pure Water	1000 cc	

Bath Condition
Plating Bath Temperature 25° ± 5°C 75
pH 3.5

65 EXAMPLE 3
Using a plating bath containing the components given in the following Table 5, a copper base plate was plated in the same manner as described in Examples 1 and 2. The

TABLE 6

					Sample	
		13	14	15	16	17
5	Plating Conditions:	Electric Current Density (A/dm ²)	1.0	1.4	1.7	2.0
	Plating Time (sec)		60	60	40	60
	Existence of Magnetic Character		X	X	0	0
	Coercive Force: Hc (Oe)		—	—	30	80
	Squareness Ratio: SQ (Br/Bs)		—	—	0.88	0.76

10 From these results, it can be understood that in this plating bath, a non-magnetic plated film was formed when the electric current density was 1.4 A/dm² or less and a ferromagnetic plated film was formed when
 15 the density was 1.7 A/dm² or more.

EXAMPLE 4

Using a plating bath containing the components given in the following Table 7, a copper base plate was plated in the same manner as described in Examples 1, 2 and 3. The plating conditions and the results

obtained are given in the following Table 8.

	Composition			
	NiSO ₄ · 7H ₂ O		140 g	25
	NiCl ₂ · 6H ₂ O		40 g	
	NH ₄ Cl		80 g	
	NaH ₂ PO ₄ · 2H ₂ O		8 g	
	Pure Water		1000 cc	

	Bath Condition			
	Plating Bath	Temperature	45° ± 5°C	30
	pH		5.5	

TABLE 8

				Sample		
		18	19	20	21	22
35	Plating Conditions:	Electric Current Density (A/dm ²)	0.8	1.2	1.5	2.0
	Plating Time (sec)		60	40	40	40
	Existence of Magnetic Character		X	X	0	0
	Coercive Force: Hc (Oe)		—	—	21	43
	Squareness Ratio: SQ (Br/Bs)		—	—	0.88	0.72

From these results, it can be understood that in this plating bath, a ferromagnetic film was obtained when the electric current density was 1.5 A/dm² or more, and a non-magnetic plated film was obtained when the density was 1.2 A/dm² or less.

EXAMPLE 5

Using a plating bath containing the components given in the following Table 9, a copper base plate was plated in the same manner as described in Examples 1, 2 and 3. The plating conditions and the results

obtained are given in the following Table 10.

	Composition			
	CoSO ₄ · 7H ₂ O		10 g	
	CoCl ₂ · 6H ₂ O		5 g	
	H ₃ BO ₃		30 g	60
	NaH ₂ PO ₄ · H ₂ O		40 g	
	Pure Water		1000 cc	

	Bath Condition			
	Plating Bath	Temperature	45°C	
	pH		5.5 ± 0.5	65

TABLE 10

			Sample	
		23	24	
70	Plating Conditions:	Electric Current Density (A/dm ²)	0.5	1.5
	Plating Time (sec)		30	10
	Existence of Magnetic Character		X	0
	Coercive Force: Hc (Oe)		—	280
	Squareness Ratio: SQ (Br/Bs)		—	0.71

75 From these results, it can be understood that in this plating bath, a ferromagnetic plated film was obtained when the electric current density was 1.5 A/dm², and a non-

magnetic plated film was obtained when the density was 0.5 A/dm².

As is apparent from the results of the above Examples, where various kinds of plat-

ing bath and base metal were used, both a non-magnetic film and ferromagnetic film were selectively obtained in a single plating bath in each case by varying the plating conditions.

When the hardness and the surface roughness of each plated film obtained were tested, no abnormalities were found, and the plated film obtained had excellent brilliance.

10 WHAT WE CLAIM IS:—

1. A method of electroplating a non-magnetic metallic coating and a ferromagnetic metallic coating on a non-magnetic metallic substrate, which comprises the steps of (a) immersing said substrate in an aqueous electroplating bath containing at least one salt of one or more ferromagnetic metals, (b) passing an electric current having a current density lying in the range of from 0.3 to 1.5 Amps/dm² between the substrate and a counter electrode in the bath to cause a non-magnetic coating to be deposited, and (c) increasing the electric current to a current density lying in the range of from 0.8 to 10 Amps/dm² to cause a ferromagnetic coating to be deposited from the same bath.
2. A method as claimed in Claim 1, wherein in the current density in step (c) is not more than 4.0 Amps/dm².
3. A method as claimed in Claim 1 or 2, wherein the ferromagnetic coating is formed by the deposition of particles having a size of 500 Å to 0.1 micron.

4. A method as claimed in Claim 1, 2 or 3, wherein the non-magnetic coating is formed by the deposition of particles having a size of 100 Å to 0.1 micron.
5. A method as claimed in any of Claims 1 to 4, wherein the ferromagnetic metal is nickel or cobalt.
6. A method as claimed in any of Claims in the electroplating bath further contains a compound of chromium and/or phosphorus.
7. A method as claimed in Claim 5 or 6, wherein the electroplating bath further contains at least one compound of copper, zinc, gold or tin.
8. A method as claimed in any preceding Claim, wherein the substrate is provided with a subbing layer of copper, zinc or tin.
9. A method of electroplating as claimed in Claim 1, substantially as hereinbefore described with reference to any of the Examples.
10. An article electroplated by a method as claimed in any preceding Claim.

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